

## WEST Search History

DATE: Wednesday, April 14, 2004

Hide?	Set Name	Query	Hit Count
		<i>DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI; THES=ASSIGNEE; PLUR=YES; OP=ADJ</i>	
<input type="checkbox"/>	L4	L1 and perfluorinat\$3 near2 ion near1 exchang\$3	9
<input type="checkbox"/>	L3	dimeriz\$5 and perfluorinat\$3 near2 ion near1 exchange	16
<input type="checkbox"/>	L2	L1 and perfluorinat\$3 near2 ion near1 exchange	9
<input type="checkbox"/>	L1	dimeriz\$5 with styrene	384

END OF SEARCH HISTORY

# WEST Search History

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DATE: Wednesday, April 14, 2004

Hide?	Set Name	Query	Hit Count
		<i>DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI; THES=ASSIGNEE; PLUR=YES; OP=ADJ</i>	
<input type="checkbox"/>	L2	L1 and perfluorinat\$3 near2 ion near1 exchange	9
<input type="checkbox"/>	L1	dimeriz\$5 with styrene	384

END OF SEARCH HISTORY

## WEST Search History

DATE: Wednesday, April 14, 2004

Hide?	Set Name	Query	Hit Count
		<i>DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI; THES=ASSIGNEE; PLUR=YES; OP=ADJ</i>	
<input type="checkbox"/>	L5	(dimerization with styrene).ti.	36
<input type="checkbox"/>	L4	L1 and perfluorinat\$3 near2 ion near1 exchange\$3	9
<input type="checkbox"/>	L3	dimeriz\$5 and perfluorinat\$3 near2 ion near1 exchange	16
<input type="checkbox"/>	L2	L1 and perfluorinat\$3 near2 ion near1 exchange	9
<input type="checkbox"/>	L1	dimeriz\$5 with styrene	384

END OF SEARCH HISTORY

## Hit List

Clear	Generate Collection	Print	Fwd Refs	Bkwd Refs
Generate OACS				

Search Results - Record(s) 1 through 9 of 9 returned.

☐ 1. Document ID: US 20040068146 A1

Using default format because multiple data bases are involved.

L2: Entry 1 of 9

File: PGPB

Apr 8, 2004

PGPUB-DOCUMENT-NUMBER: 20040068146  
PGPUB-FILING-TYPE: new  
DOCUMENT-IDENTIFIER: US 20040068146 A1

TITLE: Sol-gel derived porous microcomposite of perfluorinated ion-exchange polymer and metal oxide

PUBLICATION-DATE: April 8, 2004

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Harmer, Mark Andrew	Wilmington	DE	US	
Sun, Qun	Wilmington	DE	US	

US-CL-CURRENT: 568/303; 502/402, 502/407

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC	Draw. De
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☐ 2. Document ID: US 20030176729 A1

L2: Entry 2 of 9

File: PGPB

Sep 18, 2003

PGPUB-DOCUMENT-NUMBER: 20030176729  
PGPUB-FILING-TYPE: new  
DOCUMENT-IDENTIFIER: US 20030176729 A1

TITLE: Sol-gel derived porous microcomposite of perfluorinated ion-exchange polymer and metal oxide

PUBLICATION-DATE: September 18, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Harmer, Mark Andrew	Wilmington	DE	US	
Sun, Qun	Wilmington	DE	US	

APPL-NO: 10/ 322786 [PALM]  
DATE FILED: December 18, 2002

## RELATED-US-APPL-DATA:

Application 10/322786 is a division-of US application 09/670530, filed September 27, 2000, US Patent No. 6515190  
Application 09/670530 is a division-of US application 09/324931, filed June 3, 1999, US Patent No. 6160190  
Application 09/324931 is a division-of US application 09/121106, filed July 23, 1998, US Patent No. 5948946  
Application 09/121106 is a division-of US application 08/574751, filed December 19, 1995, US Patent No. 5824622  
Application 08/574751 is a continuation-in-part-of US application 08/362063, filed December 22, 1994, ABANDONED  
Application 08/362063 is a continuation-in-part-of US application 08/180250, filed January 12, 1994, ABANDONED

## FOREIGN-APPL-PRIORITY-DATA:

COUNTRY	APPL-NO	DOC-ID	APPL-DATE
WO	PCT/US95/00012	1995WO-PCT/US95/00012	January 10, 1995

INT-CL: [07] C07 C 21/08, C07 C 67/04, B01 J 31/00

US-CL-PUBLISHED: 560/241; 568/672, 568/927, 585/429, 502/159  
US-CL-CURRENT: 560/241; 502/159, 568/672, 568/927, 585/429

REPRESENTATIVE-FIGURES: 1

## ABSTRACT:

Porous microcomposites have been prepared from perfluorinated ion-exchange polymer and metal oxides such as silica using the sol-gel process. Such microcomposites possess high surface area and exhibit extremely high catalytic activity.

[0001] This application is a continuation-in-part of application Ser. No. 08/362,063, filed Dec. 22, 1994, which is a continuation-in-part of application Ser. No. 08/180,250, filed Jan. 12, 1994, now abandoned.

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC	Draw De
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☐ 3. Document ID: US 6680406 B2

L2: Entry 3 of 9

File: USPT

Jan 20, 2004

US-PAT-NO: 6680406  
DOCUMENT-IDENTIFIER: US 6680406 B2

TITLE: Sol-gel derived porous microcomposite of perfluorinated ion-exchange polymer and metal oxide

DATE-ISSUED: January 20, 2004

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Harmer; Mark Andrew	Wilmington	DE		
Sun; Qun	Wilmington	DE		

## ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
E. I. du Pont de Nemours and Company	Wilmington	DE			02

APPL-NO: 10/ 322786 [PALM]  
 DATE FILED: December 18, 2002

## PARENT-CASE:

CROSS REFERENCE TO RELATED APPLICATIONS This application is a divisional of application Ser. No. 09/670,530, filed Sep. 27, 2000, now U.S. Pat. No. 6,515,140, which is a divisional of application Ser. No. 09/324,931, filed Jun. 3, 1999, now U.S. Pat. No. 6,160,190 issued Dec. 12, 2000, which is a divisional of application Ser. No. 09/121,106 filed Jul. 23, 1998, now U.S. Pat. No. 5,948,946 issued Sep. 7, 1999, which is a divisional of application Ser. No. 08/574/751 filed Dec. 19, 1995, now U.S. Pat. No. 5,824,622 issued Oct. 20, 1998, which is a continuation-in-part of application Ser. No. 08/362,063 filed Dec. 22, 1994, now abandoned, which is a continuation-in-part of application Ser. No. 08/180,250 filed Jan. 12, 1994, now abandoned.

## FOREIGN-APPL-PRIORITY-DATA:

COUNTRY	APPL-NO	APPL-DATE
US	PCT/US95/00012	January 10, 1995

INT-CL: [07] C07 C 67/24, C07 C 43/11, C08 G 63/06, C08 G 59/00

US-CL-ISSUED: 560/240; 528/361, 528/417, 568/617

US-CL-CURRENT: 560/240; 528/361, 528/417, 568/617

FIELD-OF-SEARCH: 560/240, 528/361, 528/417, 568/617

## PRIOR-ART-DISCLOSED:

## U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
3151179	September 1964	Kennedy et al.	260/683.2
<u>3506635</u>	April 1970	Anderson	260/88.3
<u>3920765</u>	November 1975	Frech et al.	260/683.2
<u>4038213</u>	July 1977	McClure et al.	252/430
<u>4041090</u>	August 1977	McClure	260/671R
<u>4056578</u>	November 1977	McClure et al.	260/683.47
<u>4065515</u>	December 1977	McClure et al.	260/683.68
<u>4414409</u>	November 1983	Waller	560/233
<u>4433082</u>	February 1984	Grot	524/755
<u>4661411</u>	April 1987	Martin et al.	428/421.2
<u>4791081</u>	December 1988	Childress et al.	502/62
<u>5086085</u>	February 1992	Pekala	521/187

5094955	March 1992	Butt et al.	502/402
5252654	October 1993	David et al.	524/414
5472926	December 1995	Gubitosa et al.	502/337

## FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0 288 295	October 1988	EP	
0324080	July 1989	EP	
0 338 309	October 1989	EP	
0367408	May 1990	EP	
0503688	September 1992	EP	
1.248.426	December 1960	FR	

## OTHER PUBLICATIONS

Mauritz, K.A. et al., Polym. Mater. Sci. Eng., 58, 1079-1082, 1988.  
Olah, G. A. et al., Synthesis, 513-531, 1986.  
Waller, F.J., Catal. Rev.-Sci. Eng., 1-12, 1986.  
Weaver, J.D. et al., Catalysis Today, 14, 195-210, 1992.  
Mauritz, K.A. et al., Multiphase Polymers: Blends and Ionomers, American Chemical Society, 401-417, Chapter 16, 1989.  
Waller, F.J. et al. Chemtech, 438-441 (Jul. 1987).  
Waller, F.J., In Polymeric Reagents and Catalysts, Ford, W.T. (Ed.), Chap. 3, ACS Symposium Series 308, ACS, Washington, DC (1986).  
Martin, C.R. et al., Anal. Chem. 54, 1639-1641 (1982).

ART-UNIT: 1621

PRIMARY-EXAMINER: Parsa; J.

## ABSTRACT:

Porous microcomposites have been prepared from perfluorinated ion-exchange polymer and metal oxides such as silica using the sol-gel process. Such microcomposites possess high surface area and exhibit extremely high catalytic activity.

3 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	KMIC	Draw. D
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☐ 4. Document ID: US 6515190 B1

L2: Entry 4 of 9

File: USPT

Feb 4, 2003

US-PAT-NO: 6515190

DOCUMENT-IDENTIFIER: US 6515190 B1

TITLE: Sol-gel derived porous microcomposite of perfluorinated ion-exchange polymer and metal oxide

DATE-ISSUED: February 4, 2003

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Harmer; Mark Andrew	Wilmington	DE		
Sun; Qun	Wilmington	DE		

## ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
E. I. du Pont de Nemours and Company	Wilmington	DE			02

APPL-NO: 09/ 670530 [PALM]

DATE FILED: September 27, 2000

## PARENT-CASE:

This is a division of Application No. 09/324,931 filed Jun. 3, 1999, now U.S. Pat. No. 6,160,190, which is a division of Application No. 09/121,106 filed Jul. 23, 1998, now U.S. Pat. No. 5,948,946, which is a division of Application No. 08/574,751 filed Dec. 19, 1995, now U.S. Pat. No. 5,824,622, which is a continuation-in-part of Application No. 08/362,063 filed Dec. 22, 1994, now abandoned, which is a continuation-in-part of Application No. 08/180,250 filed Jan. 12, 1994, now abandoned.

INT-CL: [07] C07 C 205/00

US-CL-ISSUED: 568/939; 568/927

US-CL-CURRENT: 568/939; 568/927

FIELD-OF-SEARCH: 568/927, 568/939

## PRIOR-ART-DISCLOSED:

## U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3151179</u>	September 1964	Kennedy et al.	260/683.2
<u>3506635</u>	April 1970	Anderson	260/88.3
<u>3920765</u>	November 1975	Frech et al.	260/683.2
<u>4038213</u>	July 1977	McClure et al.	252/430
<u>4041090</u>	August 1977	McClure	260/671R
<u>4056578</u>	November 1977	McClure et al.	260/683.47
<u>4065515</u>	December 1977	McClure et al.	260/683.68
<u>4234470</u>	November 1980	Lawrence	568/939
<u>4414409</u>	November 1983	Waller	560/233
<u>4433082</u>	February 1984	Grot	524/755
<u>4661411</u>	April 1987	Martin et al.	428/421.2
<u>4791081</u>	December 1988	Childress et al.	502/62
<u>5086085</u>	February 1992	Pekala	521/187
<u>5094955</u>	March 1992	Butt et al.	502/402
<u>5252654</u>	October 1993	David et al.	524/414
<u>5472926</u>	December 1995	Gubitosa et al.	502/337



## FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0 288 295	October 1988	EP	
0324080	July 1989	EP	
0 338 309	October 1989	EP	
0367408	May 1990	EP	
0503688	September 1992	EP	
1.248.426	December 1960	FR	

## OTHER PUBLICATIONS

Mauritz, K.A. et al., Polym. Mater. Sci. Eng., 58, 1079-1082, 1988.  
Olah, G. A. et al., Synthesis, 513-531, 1986.  
Waller, F.J., Catal. Rev.-Sci. Eng., 1-12, 1986.  
Weaver, J.D. et al., Catalysis Today, 14, 195-210, 1992.  
Mauritz, K.A. et al., Multiphase Polymers: Blends and Ionomers, American Chemical Society, 401-417, Chapter 16, 1989.  
Waller, F.J. et al. Chemtech, 438-441 (Jul. 1987).  
Waller, F.J., In Polymeric Reagents and Catalysts, Ford, W.T. (Ed.), Chap. 3, ACS Symposium Series 308, ACS, Washington, DC (1986).  
Martin, C.R. et al., Anal. Chem. 54, 1639-1641 (1982).

ART-UNIT: 1621

PRIMARY-EXAMINER: Parsa; J.

## ABSTRACT:

Porous microcomposites have been prepared from perfluorinated ion-exchange polymer and metal oxides such as silica using the sol-gel process. Such microcomposites possess high surface area and exhibit extremely high catalytic activity.

4 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw. De
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☐ 5. Document ID: US 6160190 A

L2: Entry 5 of 9

File: USPT

Dec 12, 2000

US-PAT-NO: 6160190

DOCUMENT-IDENTIFIER: US 6160190 A

TITLE: Alkylation of aromatic compounds using a sol-gel derived porous microcomposite of perfluorinated ion-exchange polymer and metal oxide

DATE-ISSUED: December 12, 2000

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Harmer; Mark Andrew	Wilmington	DE		

Sun; Qun

Wilmington

DE

## ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE	CODE
E. I. du Pont de Nemours and Company	Wilmington	DE				02

APPL-NO: 09/ 324931 [PALM]

DATE FILED: June 3, 1999

## PARENT-CASE:

This is a division of application Ser. No. 09/121,106, filed Jul. 23, 1998 U.S. Pat. No. 5,948,946 which is a division of application Ser. No. 08/574,751, filed Dec. 19, 1995 now U.S. Pat. No. 5,824,622, which is a continuation-in-part of application Ser. No. 08/362,063, filed Dec. 22, 1994, abandoned, which is a continuation-in-part of application Ser. No. 08/180,250, filed Jan. 12, 1994, now abandoned.

INT-CL: [07] C07 C 2/66, C07 C 2/70, C07 C 2/68

US-CL-ISSUED: 585/458; 585/462, 585/467

US-CL-CURRENT: 585/458; 585/462, 585/467

FIELD-OF-SEARCH: 585/458, 585/462

## PRIOR-ART-DISCLOSED:

## U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3151179</u>	September 1964	Kennedy et al.	260/683.2
<u>3506635</u>	April 1970	Anderson	260/88.3
<u>3920765</u>	November 1975	Frech et al.	260/683.2
<u>4022847</u>	May 1977	McClure	585/458
<u>4038213</u>	July 1977	McClure et al.	252/430
<u>4041090</u>	August 1977	McClure	260/671R
<u>4056578</u>	November 1977	McClure et al.	260/683.47
<u>4060565</u>	November 1977	McClure et al.	585/462
<u>4065515</u>	December 1977	McClure et al.	260/683.68
<u>4288646</u>	September 1981	Olah	585/458
<u>4316997</u>	February 1982	Vaughan	585/458
<u>4317949</u>	March 1982	Vaughan	585/458
<u>4414409</u>	November 1983	Waller	560/233
<u>4433082</u>	February 1984	Grot	524/755
<u>4446329</u>	May 1984	Waller	585/458
<u>4547474</u>	October 1985	Olah	585/458
<u>4547604</u>	October 1985	Olah	585/458
<u>4613723</u>	September 1986	Olah	585/458
<u>4661411</u>	April 1987	Martin et al.	428/421.2
<u>4673769</u>	June 1987	Farcasiu	585/458
<u>4791081</u>	December 1988	Childress et al.	502/62

<u>4938566</u>	July 1990	Wieserman et al.	502/407
<u>4994429</u>	February 1991	Wieserman et al.	502/401
<u>5037795</u>	August 1991	Wieserman et al.	502/407
<u>5086085</u>	February 1992	Pekala	521/187
<u>5094995</u>	March 1992	Butt et al.	502/402
<u>5105047</u>	April 1992	Waller	585/458
<u>5110778</u>	May 1992	Olah	585/458
<u>5124299</u>	June 1992	Waller	502/159
<u>5252654</u>	October 1993	David et al.	524/414
<u>5430212</u>	July 1995	Butt et al.	585/526
<u>5472926</u>	December 1995	Gubitosa et al.	502/337
<u>5607890</u>	March 1997	Chen et al.	502/202
<u>5824622</u>	October 1998	Harmer et al.	502/407
<u>5948946</u>	September 1999	Harmer et al.	585/669

## FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0 288 295	October 1988	EP	
0324080	July 1989	EP	
0 338 309	October 1989	EP	
0367408	May 1990	EP	
0503688	September 1992	EP	
1248426	December 1960	FR	

## OTHER PUBLICATIONS

Mauritz, K.A. et al., Polym. Mater. Sci. Eng., 58, 1079-1082, 1988.  
Olah, G. A. et al., Synthesis, 513-531, 1986.  
Waller, F.J., Catal. Rev.-Sci. Eng., 1-12, 1986.  
Weaver, J.D. et al., Catalysis Today, 14, 195-210, 1992.  
Mauritz, K.A. et al., Multiphase Polymers: Blends and Ionomers, American Chemical Society, 401-417, Chapter 16, 1989.  
Waller, F.J. et al., Chemtech, 438-441 (Jul. 1987).  
Waller, F.J., In Polymeric Reagents and Catalysts, Ford, W.T. (Ed.), Chap. 3, ACS Symposium Series 308, ACS, Washington, DC (1986).  
Martin, C.R. et al., Anal. Chem. 54, 1639-1641 (1982).

ART-UNIT: 175

PRIMARY-EXAMINER: Bell; Mark L.

ASSISTANT-EXAMINER: Pasterczyk; J.

## ABSTRACT:

Porous microcomposites have been prepared from perfluorinated ion-exchange polymer and metal oxides such as silica using the sol-gel process. Such microcomposites possess high surface area and exhibit extremely high catalytic activity. The microcomposites catalyze, among others, the reaction between organic aromatic compounds and olefins.

3 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	KWIC	Draw De
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☐ 6. Document ID: US 6001762 A

L2: Entry 6 of 9

File: USPT

Dec 14, 1999

US-PAT-NO: 6001762

DOCUMENT-IDENTIFIER: US 6001762 A

TITLE: Reactivation of perfluorinated ion-exchange microcomposite catalysts

DATE-ISSUED: December 14, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Harmer; Mark Andrew	Wilmington	DE		
Sun; Qun	Wilmington	DE		

## ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE	CODE
E. I. du Pont de Nemours and Company	Wilmington	DE			02	

APPL-NO: 09/ 018822 [PALM]

DATE FILED: February 4, 1998

## PARENT-CASE:

This application claims the priority benefit of U.S. Provisional Application 60/040,074, filed Feb. 17, 1997.

INT-CL: [06] B01 J 37/30, B01 J 20/34

US-CL-ISSUED: 502/12; 502/27, 502/29, 502/33

US-CL-CURRENT: 502/12; 502/27, 502/29, 502/33

FIELD-OF-SEARCH: 502/12, 502/27, 502/29, 502/33, 502/56, 521/26

## PRIOR-ART-DISCLOSED:

## U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>2992189</u>	July 1961	Friedman et al.	252/413
<u>4051079</u>	September 1977	Melby	260/2.2R
<u>4800186</u>	January 1989	Tasset	502/33
<u>5824622</u>	October 1998	Harmer et al.	502/407

## FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
WO 95/19222	July 1995	WO	
WO 96/19288	June 1996	WO	

## OTHER PUBLICATIONS

Barbara Kanegsberg, Precision cleaning without ozone depleting chemicals, Chemistry & Industry, 787-791, Oct. 21, 1996.

ART-UNIT: 282

PRIMARY-EXAMINER: Niebling; John F.

ASSISTANT-EXAMINER: Ghyka; Alexander G.

## ABSTRACT:

Catalyst comprising a perfluorinated ion-exchange microcomposite can be reactivated upon contact with at least one cleaning agent, such as an oxidizing agent, organic solvent, supercritical fluid or detergent. The process may further comprise heating prior to, during or after contact followed by washing with water and/or an organic solvent.

7 Claims, 0 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw. De
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☐ 7. Document ID: US 5958822 A

L2: Entry 7 of 9

File: USPT

Sep 28, 1999

US-PAT-NO: 5958822

DOCUMENT-IDENTIFIER: US 5958822 A

TITLE: Modified fluorosulfonic acids

DATE-ISSUED: September 28, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Beckerbauer; Richard	Wilmington	DE		
Harmer; Mark Andrew	Wilmington	DE		
Sun; Qun	Wilmington	DE		

## ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE	CODE
E. I. du Pont de Nemours and Company	Wilmington	DE			02	

APPL-NO: 09/ 043367 [PALM]

DATE FILED: March 16, 1998

PARENT-CASE:

This application is the national filing under 35 U.S.C. 371 of International Application No. PCT/US96/14625, filed Sep. 12, 1996, which claims the priority benefit of U.S. Provisional Application 60/005,657, filed Sep. 19, 1995.

## PCT-DATA:

APPL-NO	DATE-FILED	PUB-NO	PUB-DATE	371-DATE	102(E)-DATE
PCT/US96/14625	September 12, 1996	WO97/11081	Mar 27, 1997	Mar 16, 1998	Mar 16, 1998

INT-CL: [06] B01 J 31/40, B01 J 27/53, C07 F 7/04, C07 C 315/04

US-CL-ISSUED: 502/168; 502/151, 502/217, 556/428, 560/231, 568/32

US-CL-CURRENT: 502/168; 502/151, 502/217, 556/428, 560/231, 568/32

FIELD-OF-SEARCH: 502/151, 502/168, 502/217, 556/428, 568/32, 560/231

## PRIOR-ART-DISCLOSED:

## U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>5093451</u>	March 1992	Panster et al.	528/9
<u>5130396</u>	July 1992	Panster et al.	528/9
<u>5239033</u>	August 1993	Panster et al.	528/9
<u>5380791</u>	January 1995	Panster et al.	524/837

## FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
2084967	June 1993	CA	
2103653	February 1994	CA	
548 821	June 1993	EP	
4 024 720	February 1991	DE	
WO 95/19222	July 1995	WO	

## OTHER PUBLICATIONS

F.J. Waller et al., "Catalysis with Nafion.RTM.", Chem. Tech., 1987, 17, 438-441.  
G.A. Clark et al., "Perfluorinated resin sulfonic acid (Nation.RTM., H.sup.T) Catalysis", Synthesis, 1986, 513-531.  
J.S. Beck et al., "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates", J. Am Chem. Soc., 1992, 114, 10834-10843.  
G. A. Bargigia et al., "Perfluoro-w-iodo-3-oxaalkanesulfonyl fluorides as Intermediates for Surfactants and Vinyl Compounds", J. Of Fluorine Chem., 19, 403-410, 1982.  
Degussa publication, "Polymers and Cataysis--The DELOXAN.RTM. Product Family", pp. 1-6.

ART-UNIT: 161

PRIMARY-EXAMINER: Geist; Gary

ASSISTANT-EXAMINER: Davis; Brian J.

## ABSTRACT:

This invention concerns modified fluorosulfonic acid compounds possessing a sulfonic acid fluoride, chloride or ester group or a sulfonic acid or a salt of a sulfonic acid group at one end and respectively a hydrolyzable or hydrolyzed silane group at the other end, said sulfonic group being adjacent a substantially fluorinated bidentate hydrocarbylene group which is in turn adjacent to a hydrocarbylenegroup linked to said hydrolyzable or hydrolyzed silane group. Self-condensation of the latter compounds provides novel siloxanes and polysiloxanes. This invention further concerns novel composites comprising a metal oxide network having incorporated therein a group having the formula:  $--O).sub.q Si(OH).sub.n-q R.sup.1.sub.m R.sup.2 R.sub.f SO.sub.3 Q$ , and compositions comprising a solid material having a reactive surface to which surface is attached at least one group having the formula:  $--O).sub.q Si(OH).sub.n-q R.sup.1.sub.m R.sup.2 R.sub.f SO.sub.3 Q$ .

35 Claims, 0 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KVMC	Draw. D.
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☐ 8. Document ID: US 5948946 A

L2: Entry 8 of 9

File: USPT

Sep 7, 1999

US-PAT-NO: 5948946

DOCUMENT-IDENTIFIER: US 5948946 A

TITLE: Use of sol-gel derived porous micropositive of perfluorinated ion-exchange polymer and metal oxide to isomerize terminal olefins

DATE-ISSUED: September 7, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Harmer; Mark Andrew	Wilmington	DE		
Sun; Qun	Wilmington	DE		

## ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE	CODE
E. I. du Pont de Nemours and Company	Wilmington	DE				02

APPL-NO: 09/ 121106 [PALM]

DATE FILED: July 23, 1998

## PARENT-CASE:

This is a of division of application Ser. No. 08/574,751 filed Dec. 19, 1995, now U.S. Pat. No. 5,824,622, which is a continuation-in-part of application Ser. No. 08/362,063, filed Dec. 22, 1994, abandoned, which is a continuation-in-part of application Ser. No. 08/180,250, filed Jan. 12, 1994, now abandoned.

INT-CL: [06] C07 C 5/23, C07 C 5/25

US-CL-ISSUED: 585/669; 585/664, 585/666, 585/670  
US-CL-CURRENT: 585/669; 585/664, 585/666, 585/670

FIELD-OF-SEARCH: 585/664, 585/666, 585/669, 585/670

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3151179</u>	September 1964	Kennedy et al.	260/683.2
<u>3506635</u>	April 1970	Anderson	260/88.3
<u>3920765</u>	November 1975	Frech et al.	260/683.2
<u>4038213</u>	July 1977	McClure et al.	252/430
<u>4041090</u>	August 1977	McClure	260/671R
<u>4056578</u>	November 1977	McClure et al.	260/683.47
<u>4065515</u>	December 1977	McClure et al.	260/683.68
<u>4414409</u>	November 1983	Waller	560/233
<u>4433082</u>	February 1984	Grot	524/755
<u>4661411</u>	April 1987	Martin et al.	428/421.2
<u>4791081</u>	December 1988	Childress et al.	502/62
<u>5086085</u>	February 1992	Pekala	521/187
<u>5094955</u>	March 1992	Butt et al.	502/402
<u>5252654</u>	October 1993	David et al.	524/414
<u>5472926</u>	December 1995	Gubitosa et al.	502/337
<u>5824622</u>	October 1998	Harmer et al.	502/407

FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0 288 295	October 1988	EP	
0324080	July 1989	EP	
0 338 309	November 1989	EP	
0367408	May 1990	EP	
0503688	September 1992	EP	
1248426	December 1960	FR	

OTHER PUBLICATIONS

Mauritz, K.A. et al., Polym. Mater. Sci. Eng., 58, 1079-1082, 1988.  
Olah, G. A. et al., Synthesis, 513-531, 1986.  
Waller, F.J., Catal. Rev.-Sci. Eng., 1-12, 1986.  
Weaver, J.D. et al., Catalysis Today, 14, 195-210, 1992.  
Mauritz, K.A. et al., Multiphase Polymers: Blends and Ionomers, American Chemical Society, 401-417, Chapter 16, 1989.  
Waller, F.J. et al. Chemtech, 438-441 (Jul. 1987).  
Waller, F.J., In Polymeric Reagents and Catalysts, Ford, W.T. (Ed.), Chap. 3, ACS Symposium Series 308, ACS, Washington, DC (1986).



Martin, C.R. et al., Anal. Chem. 54, 1639-1641 (1982).

ART-UNIT: 175

PRIMARY-EXAMINER: Bell; Mark L.

ASSISTANT-EXAMINER: Pasterczyk; J.

ABSTRACT:

Porous microcomposites have been prepared from perfluorinated ion-exchange polymer and metal oxides such as silica using a sol-gel process. Such microcomposites possess high surface area and exhibit extremely high catalytic activity. Isomerization of terminal olefins is possible with such porous microcomposites.

15 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference	See Also	Related	Claims	KWIC	Draw. Des.
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☐ 9. Document ID: US 5824622 A

L2: Entry 9 of 9

File: USPT

Oct 20, 1998

US-PAT-NO: 5824622

DOCUMENT-IDENTIFIER: US 5824622 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Porous microcomposite of perfluorinated ion-exchange polymer and metal oxide, a network of silica, or a network of metal oxide and silica derived via a sol-gel process

DATE-ISSUED: October 20, 1998

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Harmer; Mark Andrew	Wilmington	DE		
Sun; Qun	Wilmington	DE		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE	CODE
E. I. du Pont de Nemours and Company	Wilmington	DE			02	

APPL-NO: 08/ 574751 [PALM]

DATE FILED: December 19, 1995

PARENT-CASE:

This application is a continuation-in-part of application Ser. No. 08/362,063, filed Dec. 22, 1994 now abandoned, which is a continuation-in-part of application Ser. No. 08/180,250, filed Jan. 12, 1994, now abandoned.

INT-CL: [06] B01 J 20/26, B01 J 20/00, B01 J 20/10, B01 J 20/12

US-CL-ISSUED: 502/407; 502/402, 502/415, 502/158, 502/159, 502/234, 502/237

US-CL-CURRENT: 502/407; 502/158, 502/159, 502/234, 502/237, 502/402, 502/415

FIELD-OF-SEARCH: 502/158, 502/159, 502/234, 502/237, 502/319, 502/338, 502/349, 502/350, 502/355, 502/402, 502/407, 502/415

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3151179</u>	September 1964	Kennedy et al.	260/683.2
<u>3506635</u>	April 1970	Anderson	260/88.3
<u>4038213</u>	July 1977	McClure et al.	252/430
<u>4041090</u>	August 1977	McClure	260/671R
<u>4056578</u>	November 1977	McClure et al.	260/683.47
<u>4065515</u>	December 1977	McClure et al.	260/683.68
<u>4414409</u>	November 1983	Waller	560/233
<u>4433082</u>	February 1984	Grot	524/755
<u>4661411</u>	April 1987	Martin et al.	428/421.2
<u>4791087</u>	December 1988	Childress et al.	502/62
<u>4938566</u>	July 1990	Wieserman et al.	502/407
<u>4994429</u>	February 1991	Wieserman et al.	502/407
<u>5086085</u>	February 1992	Pekala	521/187
<u>5094995</u>	March 1992	Butt et al.	502/402
<u>5105047</u>	April 1992	Waller	502/402
<u>5124299</u>	June 1992	Waller	502/159
<u>5252654</u>	October 1993	David et al.	524/414
<u>5338430</u>	August 1994	Parsonage et al.	204/412
<u>5430212</u>	July 1995	Butt et al.	585/526
<u>5472926</u>	December 1995	Gubitosa et al.	502/337
<u>5607890</u>	March 1997	Chen et al.	502/238

FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0 288 295	October 1988	EP	
0324080	July 1989	EP	
0 338 309	October 1989	EP	
0367408	May 1990	EP	
0503688	September 1992	EP	
1.248.426	December 1960	FR	

OTHER PUBLICATIONS

H. Abruna, Coord. Chem. Rev., vol. 86, pp. 135-189, 1988.  
Mauritz, K.A. et al., Polym. Mater. Sci. Eng., 58, 1079-1082, 1988.  
Olah, G. A. et al., Synthesis, 513-531, 1986.  
Waller, F.J., Catal. Rev.-Sci. Eng., 1-12, 1986.

Weaver, J.D. et al., Catalysis Today, 14, 195-210, 1992.  
Mauritz, K.A. et al., Multiphase Polymers: Blends and Ionomers, American Chemical Society, 401-417, Chapter 16, 1989.  
Waller, F.J. et al. Chemtech, 438-441 (Jul. 1987).  
Waller, F.J., In Polymeric Reagents and Catalysts, Ford, W.T. (Ed.), Chap. 3, ACS Symposium Series 308, ACS, Washington, DC (1986).  
Martin, C.R. et al., Anal. Chem. 54, 1639-1641 (1982).

ART-UNIT: 175

PRIMARY-EXAMINER: Bell; Mark L.

ASSISTANT-EXAMINER: Pasterczyk; J.

ABSTRACT:

Porous microcomposites comprising a perfluorinated ion-exchange polymer (PFIEP) containing pendant sulfonic acid and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, a network of silica, or a network of metal oxide and silica are prepared from PFIEP and one or more precursors selected from the group consisting of a metal oxide precursor, a silica precursor, and a metal oxide and silica precursor using an in situ process. Such microcomposites have a first set of pores having a pore size diameter ranging from about 0.5 nm to about 75 nm and may further comprise a second set of pores having a diameter ranging from about 75 nm to about 1000 nm. These microcomposites possess high surface area and exhibit high catalytic activity for a variety of reactions including, but not limited to, nitrations, esterifications, dimerizations, alkylations, polymerizations, acylations, and isomerizations.

16 Claims, 1 Drawing figures

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWC	Drawn De
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Clear	Generate Collection	Print	Fwd Refs	Bkwd Refs	Generate OACS
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Term	Documents
ION	1364347
IONS	503895
EXCHANGE	724195
EXCHANGES	55227
PERFLUORINAT\$3	0
PERFLUORINAT	8
PERFLUORINATBD	1
PERFLUORINATCD	3
PERFLUORINATD	3
PERFLUORINATDD	1
PERFLUORINATE	68
(L1 AND PERFLUORINAT\$3 NEAR2 ION NEAR1 EXCHANGE).PGPB,USPT,USOC,EPAB,JPAB,DWPI.	9

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NEWS 9 MAR 29 Pharmaceutical Substances (PS) now available on STN  
NEWS 10 MAR 29 WPIFV now available on STN  
NEWS 11 MAR 29 No connect hour charges in WPIFV until May 1, 2004  
NEWS 12 MAR 29 New monthly current-awareness alert (SDI) frequency in RAPRA  
  
NEWS EXPRESS MARCH 31 CURRENT WINDOWS VERSION IS V7.00A, CURRENT  
MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),  
AND CURRENT DISCOVER FILE IS DATED 3 MARCH 2004  
  
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182418 DIMER?

4672 PERFLUORINAT?

1043311 ION

658873 IONS

1388268 ION

(ION OR IONS)

137 PERFLUORINAT? ION

(PERFLUORINAT? (W) ION)

L1 7 DIMER? AND PERFLUORINAT? ION

=> s dimer? and perfluorinat?

182418 DIMER?

4672 PERFLUORINAT?

L2 104 DIMER? AND PERFLUORINAT?

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253068 STYRENE

4258 STYRENES

254105 STYRENE

(STYRENE OR STYRENES)

L3 2 L2 AND STYRENE

=> s l1 or l3

L4 8 L1 OR L3

=> d l4 ibib ab 1-8

L4 ANSWER 1 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1998:689189 CAPLUS

DOCUMENT NUMBER: 129:318232

TITLE: Porous microcomposite of **perfluorinated ion**-exchange polymer and dispersed metal oxide and/or silica derived via a sol-gel process

INVENTOR(S): Harmer, Mark Andrew; Sun, Qun

PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA

SOURCE: U.S., 24 pp., Cont.-in-part of U.S. Ser. No. 362,063,

abandoned.  
CODEN: USXXAM

DOCUMENT TYPE: Patent  
LANGUAGE: English  
FAMILY ACC. NUM. COUNT: 4  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5824622	A	19981020	US 1995-574751	19951219
ES 2139187	T3	20000201	ES 1995-907964	19950110
WO 9619288	A1	19960627	WO 1995-US16566	19951220
W: CN, JP				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
EP 799091	A1	19971008	EP 1995-944346	19951220
EP 799091	B1	19980902		
R: DE, FR, GB, IT, NL				
CN 1170373	A	19980114	CN 1995-196956	19951220
CN 1082940	B	20020417		
US 5916837	A	19990629	US 1996-683998	19960719
US 5948946	A	19990907	US 1998-121106	19980723
US 6034290	A	20000307	US 1999-277094	19990326
US 6160190	A	20001212	US 1999-324931	19990603
US 6515190	B1	20030204	US 2000-670530	20000927
US 2003176729	A1	20030918	US 2002-322786	20021218
US 6680406	B2	20040120		
US 2004068146	A1	20040408	US 2003-680838	20031007

PRIORITY APPLN. INFO.:

US 1994-180250	B2	19940112
US 1994-362063	B2	19941222
WO 1995-US12	A	19950110
US 1995-574751	A	19951219
WO 1995-US16566	W	19951220
US 1996-683998	A3	19960719
US 1998-121106	A3	19980723
US 1999-324931	A3	19990603
US 2000-670530	A3	20000927
US 2002-322786	A3	20021218

AB Porous microcomposites are described which comprise a **perfluorinated ion-exchange polymer (PFIEP)** containing pendant sulfonic acid and/or carboxylic acid groups entrapped in a highly dispersed network of metal oxide and/or silica. The microcomposites are prepared from PFIEP (especially NAFION NR 005) and  $\geq 1$  precursors selected from a metal oxide precursor (e.g., aluminum tri(sec-butoxide)) and/or a silica precursor (e.g., tetramethoxysilane) using an in situ process. The microcomposites have a first set of pores having pore size diameter 0.5-75 nm and may further comprise a second set of pores having diameter 75-1000 nm. These microcomposites possess high surface area and exhibit high catalytic activity for a variety of reactions including nitration, esterification, **dimerization**, alkylation, polymerization, acylation and isomerization.

REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1996:527339 CAPLUS

DOCUMENT NUMBER: 125:171500

TITLE: Sol-gel derived porous microcomposites of **perfluorinated ion-exchange polymer** and metal oxide as catalyst for organic reactions and their preparation

INVENTOR(S): Harmer, Mark Andrew; Sun, Qun

PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA

SOURCE: PCT Int. Appl., 59 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English  
FAMILY ACC. NUM. COUNT: 4  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9619288	A1	19960627	WO 1995-US16566	19951220
W: CN, JP				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
US 5824622	A	19981020	US 1995-574751	19951219
EP 799091	A1	19971008	EP 1995-944346	19951220
EP 799091	B1	19980902		
R: DE, FR, GB, IT, NL				
US 6034290	A	20000307	US 1999-277094	19990326

PRIORITY APPLN. INFO.:  
US 1994-362063 A 19941222  
US 1995-574751 A 19951219  
US 1994-180250 B2 19940112  
WO 1995-US12 A 19950110  
WO 1995-US16566 W 19951220  
US 1996-683998 A3 19960719

AB Porous microcomposites, having high surface area, pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout, and pore size 0.5-1000 nm, are prepared from **perfluorinated ion-exchange** polymer and metal oxides such as silica using the sol-gel process. The microcomposites are useful as catalysts for olefin isomerization, hydrocarbon alkylation, nitration or sulfonation of organic compds., etc. Thus, a 5% solution of Nafion NR 005 [.apprx.6.3:1 tetrafluoroethylene-perfluoro(3,6-dioxo-4-methyl-7-octenesulfonyl fluoride) copolymer] and a solution of tetramethoxysilane were stirred together and formed a gel in .apprx.10 s. The gel was processed and acidified giving a fine particle, light-yellow glasslike material (.apprx.13:87 Nafion-silica) having a BET surface area of 123 m<sup>2</sup>/g and average pore diameter 22 nm, which (2.5 g) was used to catalyze the isomerization of 1-butene at 50°, WHSV 0.4/h, and 2:1 He-1-butene flow, giving trans-2-butene 66.3, cis-2-butene 26.8, and 1-butene 6.9%.

L4 ANSWER 3 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1996:464450 CAPLUS

DOCUMENT NUMBER: 125:90851

TITLE: High Surface Area Nafion Resin/Silica Nanocomposites:  
A New Class of Solid Acid Catalyst

AUTHOR(S): Harmer, Mark A.; Farneth, William E.; Sun, Qun

CORPORATE SOURCE: Central Research and Development, DuPont Company,  
Wilmington, DE, 19880-0356, USA

SOURCE: Journal of the American Chemical Society (1996),  
118(33), 7708-7715  
CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

AB A novel nanocomposite of Nafion NR 50 (**perfluorinated ion-exchange** polymer) resin was prepared, in which small (20-60 nm) diameter Nafion resin particles are entrapped within a porous silica network. This material combined the excellent solid acid catalyst properties of Nafion resin with the desirable porous support characteristics of silica, with a BET surface of 150-500 mg/g. Assuming the Nafion resin particles to be dense spheres, the effective surface area of the Nafion resin alone was estd, at 153 (for 20 nm spheres) to 50 (60 nm spheres) m<sup>2</sup>/g. This material was developed using an in-situ sol-gel technique in which solns. of Nafion resin were mixed with soluble silicon sources to form a gel, which is dried to a clear hard glass-like material. These new porous nanocomposites offer the potential for significantly enhanced activity due to the increased accessibility of the Nafion resin-based acid sites. Examples of catalytic reactions were given in which the activity per unit



weight of Nafion resin were at least 100 times higher in the composite than the pure polymer alone.

L4 ANSWER 4 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1995:909497 CAPLUS  
DOCUMENT NUMBER: 123:290381  
TITLE: Sol-gel derived porous microcomposite of  
**perfluorinated ion-exchange** polymers  
and metal oxides as process catalysts  
INVENTOR(S): Harmer, Mark Andrew  
PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co., USA  
SOURCE: PCT Int. Appl., 64 PP.  
CODEN: PIXXD2  
DOCUMENT TYPE: Patent  
LANGUAGE: English  
FAMILY ACC. NUM. COUNT: 4  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9519222	A1	19950720	WO 1995-US12	19950110
W: JP				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
EP 739239	A1	19961030	EP 1995-907964	19950110
EP 739239	B1	19990915		
R: BE, CH, DE, ES, FR, GB, IT, LI, NL				
JP 09508057	T2	19970819	JP 1995-519031	19950110
ES 2139187	T3	20000201	ES 1995-907964	19950110
US 6034290	A	20000307	US 1999-277094	19990326
US 2003176729	A1	20030918	US 2002-322786	20021218
US 6680406	B2	20040120		
US 2004068146	A1	20040408	US 2003-680838	20031007

PRIORITY APPLN. INFO.:

US 1994-180250	A	19940112
US 1994-362063	A	19941222
WO 1995-US12	W	19950110
US 1995-574751	A2	19951219
WO 1995-US16566	A	19951220
US 1996-683998	A3	19960719
US 1998-121106	A3	19980723
US 1999-324931	A3	19990603
US 2000-670530	A3	20000927
US 2002-322786	A3	20021218

AB Porous microcomposites are prepared from (NAFION) **perfluorinated ion-exchange** polymers with pendant sulfonic and carboxylic acid groups and metal oxides (silica, alumina, titania, etc.) using the sol-gel process. Such microcomposites possess high surface area and exhibit extremely high catalytic activity, e.g., for nitration of aroms., esterification of acids, **styrene dimerization**, alkylation or acylation of aroms.

L4 ANSWER 5 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1994:579058 CAPLUS  
DOCUMENT NUMBER: 121:179058  
TITLE: Ethene **dimerization** using a Nafion supported  
 $\sigma$ -arylnickel(II) species  
AUTHOR(S): Seen, Andrew J.; Cavell, Kingsley J.; Mau, Albert  
W.-H.; Hodges, Alastair M.  
CORPORATE SOURCE: Chemistry Department, University of Tasmania, Hobart,  
Tasmania, 7005, Australia  
SOURCE: Journal of Molecular Catalysis (1994), 90(3), 245-56  
CODEN: JMCADS; ISSN: 0304-5102  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 121:179058

AB The cationic organonickel species,  $[\text{Ni}(\text{o-tolyl})(\text{py})_2\text{PPh}_3]^+$ , has been immobilized within the **perfluorinated ion-exchange** polymer Nafion. Immobilization was achieved by replacement of the halide and a PPh<sub>3</sub> ligand, in  $\text{Ni}(\text{o-tolyl})\text{Br}(\text{PPh}_3)_2$ , with pyridine. The strong interaction between the Nafion and the cationic species was the driving force for the reaction, the Nafion thus acting in the dual role of firstly forming and then supporting the catalyst precursor. The structure of the Nafion immobilized species was confirmed by comparison of FTIR and <sup>31</sup>P NMR spectra of the Nafion supported species with spectra for the  $[\text{Ni}(\text{o-tolyl})(\text{py})_2\text{PPh}_3]\text{PF}_6$  complex. Both the unsupported and supported species were shown to be catalytically active for ethene **dimerization**. The inability of the solvent to significantly swell the Nafion limited the catalytic activity of the supported species. Immobilization in Nafion did however extend the lifetime of the supported catalyst.

L4 ANSWER 6 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN  
ACCESSION NUMBER: 1993:236300 CAPLUS  
DOCUMENT NUMBER: 118:236300  
TITLE: Classic process chemistry. New science and new applications  
AUTHOR(S): Nugent, William A.; McKinney, Ronald J.; Hobbs, Frank W., Jr.; Waller, Francis J.  
CORPORATE SOURCE: Cent. Res. Dev. Dep., E. I. Du Pont de Nemours and Co., Wilmington, DE, 19880-0328, USA  
SOURCE: Advances in Chemistry Series (1992), 230 (Homogeneous Transition Met. Catal. React.), 479-89  
CODEN: ADCSAJ; ISSN: 0065-2393  
DOCUMENT TYPE: Journal; General Review  
LANGUAGE: English

AB A review with 53 refs. on Ni-catalyzed hydrocyanation modified to provide an efficient route to anti-inflammatory drugs, on Cu salt-treated **perfluorinated ion-exchanger** polymers to provide cyclopropanation catalysts for manufacture of pyrethroid insecticides, and on catalytic **dimerization** of Me acrylate and tandem conjugate addition-cyclization of the **dimers** to provide a simple route to 2,3-disubstituted cyclopentanones.

L4 ANSWER 7 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN  
ACCESSION NUMBER: 1992:511122 CAPLUS  
DOCUMENT NUMBER: 117:111122  
TITLE: Simultaneous preparation and oligomerization of hexafluoropropene by fluorination of chlorofluoropropenes  
INVENTOR(S): Paleta, Oldrich; Kvicala, Jaroslav; Dedek, Vaclav  
PATENT ASSIGNEE(S): Czech.  
SOURCE: Czech., 7 pp.  
CODEN: CZXXA9  
DOCUMENT TYPE: Patent  
LANGUAGE: Czech  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 267292	B1	19900212	CS 1988-4015	19880609
PRIORITY APPLN. INFO.:			CS 1988-4015	19880609
OTHER SOURCE(S):		CASREACT 117:111122		

AB Hexafluoropropene and its oligomers  $(\text{C}_3\text{F}_6)_n$  ( $n = 1-4$ ), chemical intermediates for compds. useful in micro- and optoelectronics or for fluorinated surfactants and **perfluorinated ion** exchangers, were prepared in 1-step reaction of chlorofluoropropenes  $\text{CFX:CFCF}_2\text{Y}$  ( $\text{X}, \text{Y} = \text{Cl}, \text{F}$ ) with NaF and/or KF and/or CsF and/or Et<sub>4</sub>NF in solvents at -30 to 190°. Mixts. of com. chlorofluoropropenes could also be used as

starting materials. Thus, 10 g CF<sub>2</sub>:CFCF<sub>2</sub>Cl was added over 10 min to a stirred mixture of 12 g KF and 20 mL DMF at 0-10° and the whole was stirred for addnl. 15 min. The volatiles (5.5 g) containing 96% CF<sub>3</sub>:CFCF<sub>3</sub> (I) were separated by distillation at 25° to give a liquid residue (1.4 g) containing

65% I-dimer, 33% I-trimer, and 2% I-tetramer. In a similar experiment, fluorination-oligomerization of a mixture of CFCl:CFCF<sub>2</sub>Cl 10, CFCl:CFCF<sub>3</sub> 10, and CF<sub>2</sub>:CFCF<sub>2</sub>Cl 3 g for 9 h at 100° in the presence of 24 g KF and 0.5 g dibenzo-18-crown-6 in 20 mL N-methylpyrrolidinone, gave 9.8 g mixture containing I-dimer 16, I-trimer 68, and I-tetramer 16%.

L4 ANSWER 8 OF 8 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1979:611897 CAPLUS

DOCUMENT NUMBER: 91:211897

TITLE: Cationic oligomerization of **styrene** by solid acids. II. Oligomerization of **styrene** catalyzed by **perfluorinated** resinsulfonic acid (nafion-H)

AUTHOR(S): Hasegawa, Hiroshi; Higashimura, Toshinobu

CORPORATE SOURCE: Dep. Polym. Chem., Kyoto Univ., Kyoto, 606, Japan

SOURCE: Polymer Journal (Tokyo, Japan) (1979), 11(9), 737-43

CODEN: POLJB8; ISSN: 0032-3896

DOCUMENT TYPE: Journal

LANGUAGE: English

AB The reactivity of catalysts and mol. weight distribution products were compared in the cationic oligomerization of **styrene** in presence of solid Nafion H (I) [63937-00-8] or in presence of soluble CF<sub>3</sub>SO<sub>3</sub>H. Oligomers consisting of **dimer** to hexamer were obtained with I, whereas a linear **dimer** was the main product with CF<sub>3</sub>SO<sub>3</sub>H in nonpolar solvents at 50-70°. As superacid solid catalyst, I had the following characteristics: (1)retention of catalytic activity on repeated reaction and the absence of a limiting yield; (2)higher activity than that of a conventional poly(styrenesulfonic acid) resin; (3)virtual absence of solvent effects on the reaction rate and product composition; and (4)formation of Friedel-Crafts adducts between **styrene** and an aromatic solvent.